

Calcium Effect on Arsenic (V) Adsorption onto Coal Fly Ash

Tian Wang¹, Tingzhi Su¹, Jianmin Wang¹, Ken Ladwig²

¹ Department of Civil, Architectural & Environmental Engineering, University of Missouri – Rolla, Rolla, MO 65409; ² Electric Power Research Institute (EPRI), 3420 Hillview Ave., Palo Alto, CA 94304

KEYWORDS: arsenic, calcium, adsorption, fly ash

ABSTRACT

Batch tests indicated that arsenic (As) leaching is significantly affected by the calcium concentration in fly ash in the alkaline pH range. Arsenic leaching from low calcium fly ash from eastern bituminous coal increased with increase of pH in the alkaline pH range (pH 7 – 12). Fly ash from eastern bituminous coal with a slightly higher calcium content exhibited an arsenic leaching peak at pH 9, followed by decreased arsenic leaching up to pH 12. For alkaline ashes derived from subbituminous coal with much higher calcium content, significantly less arsenic was leached in the alkaline pH range. To improve understanding of arsenic leaching behavior, batch experiments with washed ash were performed to evaluate partitioning of As(V) spiked into the system, along with different amounts of calcium addition. Results suggested that the addition of calcium significantly reduced the soluble arsenic ratio in the alkaline pH range. This phenomenon was explained by postulating the formation of two highly adsorbable neutral arsenic species, CaHAsO_4 and $\text{Ca}_3(\text{AsO}_4)_2$, in this pH range. An adsorption model was developed to quantify the calcium impact on arsenic adsorption.

INTRODUCTION

High concentrations of arsenic (As) have long been recognized to be toxic to human and animals. Long term exposure to As can cause cancer of skin, liver, lung bladder and kidney.¹ Effective January 2006, the Federal Maximum Contaminant Level (MCL) for arsenic in drinking water was revised by EPA from 50 ppb to 10 ppb.² The stricter regulation may impact alternatives for the disposal and use of arsenic containing wastes and products, including coal fly ash. Although there have been extensive studies on the general leaching characteristics of arsenic from fly ash,³⁻⁸ quantification of the calcium effect on arsenic leaching has been less well studied. Van der hoek et al.⁹ conducted batch leaching tests for one acidic and one alkaline fly ash, and observed higher arsenic concentrations at higher pH for acidic ashes, but they observed the opposite behavior for alkaline ash, indicating different leaching mechanisms. By comparing arsenic leaching behavior from fly ash with its adsorption onto the

major mineral compounds in fly ash, they concluded that arsenic leaching from acidic ash was likely to be controlled by surface complexation with iron oxide, while a calcium phase was shown to be responsible for alkaline ash. This conclusion agrees with that from Zielinski et al., who studied the mode of occurrence of arsenic in fly ash with XAFS spectroscopy.¹⁰ Results indicated that arsenic is associated with some combination of iron oxide, oxyhydroxide or sulfate in a highly acidic fly ash, but with a phase similar to calcium arsenate in a highly alkaline ash.

Several hypotheses have been proposed to explain the effect of calcium on arsenic leaching and adsorption on fly ash. One hypothesis is that arsenic is reacting with calcium and precipitates as calcium arsenate.¹¹ However, Fruchter et al.¹² and Van der hoek et al.⁹ showed that As concentrations in leachate could not be modeled on the basis of solubility. Another hypothesis is that formation of secondary minerals such as ettringite may contribute to arsenic stabilization in fly ash.¹⁴⁻¹⁶ Since the formation of ettringite only occurs at pH greater than 11, this can only explain reduced leaching at very high pH levels.¹⁵ None of these hypotheses fully explain the arsenic leaching behavior across the full pH range.

Adsorption models that incorporate surface electrostatic effects have been applied to quantify arsenic adsorption on various media, including soil, iron hydroxide and ferric sludge,^{17, 18, 13} and, in most cases, this approach works well for fitting experimental data. However, it is very complicated in terms of the number of parameters to be predicted or calibrated, and results depend heavily on the initial assumptions.⁹ It is even more difficult to apply this type of model to a system with multiple constituents interacting with each other.

Overall, calcium is known to play an important role in the release of arsenic from fly ash. The objectives of this study are to compare the leaching behavior of arsenic from several acidic and alkaline fly ashes, to explore the mechanism of calcium effect on arsenic leaching and sorption/precipitation processes on coal fly ash, and to develop a robust adsorption model to quantify arsenic partitioning in fly ash.

MATERIALS AND METHODS

Fly Ash Samples

A total of seven ash samples were used in this study, collected from three different power plants. Ashes #1004, #1005, #1008 and #1009 were all collected from one pulverized coal power plant (Plant ID 33106) burning eastern bituminous coal. The plant uses cold-side electrostatic precipitators (ESPs) to capture fly ash. Ashes #1004 and #1009 were collected from the same unit but at different times, when different eastern bituminous coals were being burned; the coal for Ash #1009 had higher calcium content. Ashes #1005 and #1008 were collected from the same plant and during the same coal burns as ashes #1004 and 1009, respectively, but from a separate unit with an ammonia-based

selective non-catalytic reduction (SNCR) system for NO_x control. Ashes #1015, #1018, and #7 were collected from power plants burning primarily subbituminous coal. Ashes #1015 and #1018 came from a cyclone boiler power plant (Plant ID 25410) with cold-side ESPs and burning a blend of 80% subbituminous and 20% bituminous coal. Ash #1018 was sampled from a unit with SNCR. Sample #7 came from a pulverized coal power plant (Plant ID 50213) with hot-side ESPs and burning 100% subbituminous coal.

In this paper, the four bituminous coal fly ashes with natural pH less than 7 are defined as acidic ashes, and the three subbituminous coal fly ash with natural pH greater than 7 were defined as alkaline ashes. The basic physical and chemical characteristics of these ashes, including natural pH, BET surface area (analyzed using Quantachrome Autosorb-1-C high performance surface area and pore size analyzer, Quantachrome Instruments, FL, USA), pH_{pzc} (analyzed using Zetasizer 3000, Malvern Instruments, Worcestershire, UK), loss-on-ignition (LOI) (determined using gravimetric methods), and total arsenic concentration are shown in Table 1. The total As in fly ash was determined using microwave-assisted acid digestion (0.4 g fly ash + 10 mL HNO₃ + 5 mL HF + 5 mL HCl) followed by graphite furnace atomic absorption (GFAA) measurement. The accuracy of the As determination was demonstrated by using a certified reference material, NIST-1633a (National Institute of Standards and Technology, USA; certified As = 145±15 mg/kg, measured As = 156.3±1.3 mg/kg). Total Ca concentration was determined using X-Ray Fluorescence Spectroscopy (X-LAB 2000, SPECTRO Analytical Instruments GmbH & Co. KG).

Batch Leaching and Batch Titration experiments

Batch leaching experiments were performed to determine the leaching behavior of arsenic from raw fly ash under different pH conditions; and batch titration experiments were employed to determine the surface site acidity and density. Detailed procedures for these two experiments are available in other papers.¹⁹⁻²⁰ Raw ash was dried and used for batch leaching experiments, while DI water washed ash was used for the titration experiments under the ionic strength of 0.01 M (NaNO₃). A solid/solution ratio (S/L) of 1:10 was used and pH was adjusted to the range of 2-12 for each group of samples. The mixture was shaken on an EBERBACH 6010 shaker for 24 hours, then allowed to settle overnight. The supernatant was collected and acidified using HNO₃ before arsenic and calcium analysis.

As(V) Partitioning with Different Calcium Additions

Batch partitioning experiments were performed to evaluate the effect of calcium on arsenic adsorption onto fly ash. In this experiment, fly ash samples were washed five times with DI water, and dried before use. The detailed washing procedure is described elsewhere.¹⁹ The solid/liquid ratio was 1:10. Ionic strength was adjusted with 0.01M NaNO₃ solution. For this study, samples were divided

into several groups, 5 mg/L of As(V) was added to all samples as adsorbate, and a series of Ca concentrations were added to the different groups. After mixing on the shaker for 24 hours, all samples were allowed to settle overnight. The supernatant was then collected for arsenic and calcium analysis. The final pH was measured using the remaining mixture in the bottle.

Analytical Method

A GFAA spectrometer (AAAnalyst 600, Perkin-Elmer Corp., Norwalk, Connecticut, USA) and a Flame Atomic Absorption Spectroscopy (FLAA; Model 3110, Perkin-Elmer Corp., Norwalk, Connecticut, USA) were used to determine arsenic and calcium concentrations in solution, respectively. An Orion PerpHecT Triode pH electrode (model 9207BN) and a pH meter (perpHecT LoR model 370) were used for pH measurement.

Data Analysis

The non-linear regression program Kaleidagraph™ (Synergy Software, 2002) was used for titration modeling to determine the surface site density and acidity constants. SigmaPlot (SPSS Inc., 2001) was used as a multi-variable nonlinear regression program to determine the adsorption constants of each arsenic species on fly ash.

RESULTS AND DISCUSSION

Arsenic and Calcium Leaching From Raw Fly Ash

Batch leaching experiments were performed with six fly ash samples. Both arsenic and calcium concentrations in the leachate were analyzed and plotted in Figure 1a and 1b respectively.

Arsenic leaching from all three acidic ashes was significantly affected by the pH as observed in Figure 1a. For ashes #1005 and #1004, arsenic release was minimal in their natural pH range, between 3 and 7. When pH is below 3, arsenic release increased significantly. On the other hand, when pH is above 7, soluble arsenic concentration was also increased. The major arsenic species in fly ash was reported to be As(V) in previous research.^{21, 22} The As(V) speciation diagram (Figure 2) indicated that the neutral H_3AsO_4 species dominates when pH is less than 2. Therefore, the neutral arsenic molecule is considered not adsorbable by ash surface. The dissolution of ash particles under very acidic conditions might also contribute to the higher soluble arsenic concentration. When pH increases to above 2, the total concentrations of anionic arsenic species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) also increase. These anions can be adsorbed by protonated ash surface site α . When pH is greater than 7, the protonated surface site α is no longer available, resulting in less arsenic adsorption on the ash surface.

Ash #1009 performed differently from the other two acidic ashes in Figure 1a. When pH was less than 9, it had a similar leaching pattern as the other two, with minimal release at pH 3-4. However, when pH was greater than 9, the soluble arsenic concentration decreased with the increase of pH, and when pH was greater than 11, the arsenic concentration began to increase again.

Unlike acidic ashes, alkaline ashes displayed very low leachability for arsenic under neutral and alkaline pH conditions (Figure 1a). One high arsenic concentration at pH 3 for ash #1018 was most likely caused by ash dissolution. Comparing the leaching results from different ashes with their physical–chemical characteristics listed in Table 1 indicates that the general arsenic leaching behavior is correlated with the calcium content in fly ash matrix. The calcium contents in the three alkaline ashes are 20-30 times greater than those in ash #1005 and #1004; acidic ash #1009 has a calcium content about twice as high as the other two acidic ashes. Correspondingly, the soluble calcium concentrations in leachates from the alkaline ashes were significantly greater than for the acidic ashes below pH 11 (Figure 1b), but were more sensitive to pH change and decreased faster with increase of pH. These results indicate that calcium leaching from alkaline ashes was a dissolution/precipitation controlled process, and the fairly low leachability of arsenic from the alkaline ashes across a broad pH range was likely associated with the precipitation or coprecipitation of arsenic with calcium phases. The situation is quite different for acidic ashes, where the soluble calcium concentration decreased smoothly with increase of pH, and arsenic leachability is more dependant on pH change. The observed correlation between arsenic leachability and calcium content in fly ashes is further evidence of the finding by Van de hoek et al.⁹ that a calcium phase in fly ash is likely to control the release and adsorption of arsenic in the alkaline pH range. The leaching mechanism of arsenic from acidic ashes will be discussed more fully in the following section.

Arsenic Partitioning in Washed Fly Ash under Different Calcium Additions

To test the effect of calcium on arsenic adsorption on fly ash, and to further investigate the leaching mechanism of arsenic from acidic fly ashes, ash #1008 and ash #1005 were selected for partitioning experiments with different calcium additions. For all partitioning experiments, the ash was washed prior to testing and 5 mg/L of As were added to the system. For ash #1008, sample bottles were divided into four groups, with calcium additions of 0 mg/L, 50 mg/L, 100 mg/l and 150 mg/L. Results are shown Figure 3. The As(V) partitioning curve without calcium addition has a similar trend as the raw ash leaching curve. Although only 5 mg/L of As(V) was added to the system, the maximum release reached 12 mg/L at pH 12, indicating that a significant amount of arsenic was released from washed fly ash. Addition of calcium significantly enhanced arsenic adsorption in pH range of 7-12, and a larger adsorption difference was observed at higher pH. For example, at pH 8 with 50 mg/L of calcium addition, 25% more arsenic was adsorbed, while at pH 11, arsenic adsorption was increased by 75%. This effect became less significant with calcium addition above 50 mg/L. The

arsenic partitioning curve in the presence of calcium is analogous to the leaching curve of raw ash #1009 (Figure 1a), suggesting a similar mechanism applies in both circumstances.

Three Ca loadings were applied to As(V) partitioning experiment with ash #1005: 0 mg/L, 100 mg/L and 500 mg/L. Results shown in Figure 4 were similar with those of ash #1008, except that soluble Ca concentration decreased sharply at pH greater than 11 with 500 mg/L Ca addition, which may be caused by precipitation of Ca(OH)₂ at high Ca loading and high pH conditions.

To determine whether the precipitation of Ca₃(AsO₄)₂ occurred at high pH in this study, the products of [Ca]³×[AsO₄]² were calculated based on the group of data with 50 mg/L of calcium addition for ash #1008. Results are listed in Table 2. Instead of one consistent solubility product (K_{sp}), the large variation of the product, up to four orders of magnitude, indicated that the arsenic release was not a calcium arsenate precipitation controlled process. Ettringite formation contributes to the stabilization of arsenic in fly ash generally in alkaline ashes, and only above pH 11, while experimental data indicated that calcium effect in these acidic ashes became observable since pH 7-8,.

The current experimental data suggest that some other mechanism is at least partially responsible for controlling arsenic release in the acidic ashes. Calcium added into the system can form complexes with arsenic in forms of CaH₂AsO₄⁺, CaHAsO₄, CaAsO₄⁻, Ca₃(AsO₄)₂.²³ It has been reported that the neutral forms of metal complexes,^{24, 25} have higher affinity to the sorbent surface. Considering the occurrence of the two neutral species CaHAsO₄ and Ca₃(AsO₄)₂ in the pH range where arsenic adsorption was enhanced, it is assumed that the adsorption of these two species contributed to the stabilization of arsenic in fly ash. This assumption is verified by the modeling process described below.

Modeling As(V) Adsorption onto Washed Ash

Surface Site Characterization

The surface site density and acidity constant of fly ash are essential parameters for metal adsorption modeling. A previously developed titration model¹⁹ was used to determine these parameters. The model is expressed as:

$$\Delta V_{SS} = \sum_i \frac{V_0 S_{Ti} K_{Hi}}{C} \left\{ \frac{1}{[H^+] + K_{Hi}} - \frac{1}{[H^+]_0 + K_{Hi}} \right\} \quad (1)$$

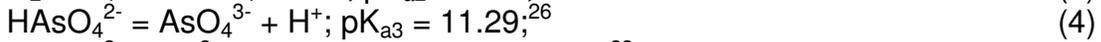
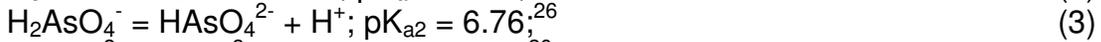
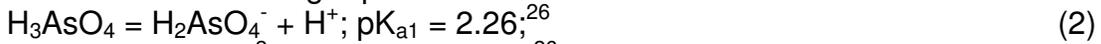
where ΔV_{SS} is the net volume of stock acid/base (negative value for acid) solution consumed by surface sites (mL); V_0 is total volume of the ash mixture (mL); S_{Ti} is the total acid site concentration of species i (M); K_{Hi} is the acidity constant of the species i (M); C is the concentration of the acid/base stock solution (M); and $[H^+]_0$ is the hydrogen ion concentration of the control unit (without acid or base addition) (M). Note that the total surface site concentration $S_{Ti} = \Gamma_i \times SS$, where Γ_i is the

surface site density for species i (mol/g-SS) and SS is the solids concentration (g/L).

After correction using the titration data for blanks, the net titration data for washed Ash #1008 with S/L ratio of 1:10 were plotted as the equilibrium pH as a function of the volume of acid (negative value) or base consumed by fly ash (mL), shown in Figure 5. KaleidaGraph™ was employed for the curve fitting. Results showed that using three surface sites can best fit the experimental data. Table 3 lists the surface site density (Γ) and acidity constant (pK_H) for each site, α , β , and γ . Since the pH_{pzc} of this ash was 6.2 (Table 1), which is between the pK_H s of the site α and site β (3.2 and 7.3, respectively), the protonated surface sites α is positively charged, denoted as $\underline{S}_1OH_2^+$, while the protonated species of the other two surface sites are in neutral form.

Modeling As(V) Adsorption

The concentrations of different As(V) species in the system can be calculated based on the following equations:

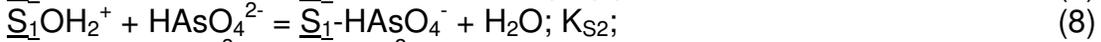
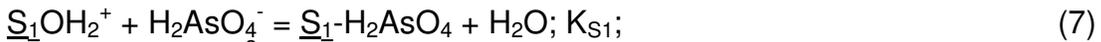


The stoichiometry of $Ca_3(AsO_4)_2$ was converted to $Ca_{1.5}AsO_4$, to simplify the adsorption equations. K_{a4} and K_{a5} are the formation constants of $CaHAsO_4$ and $Ca_3(AsO_4)_2$, respectively. K_{a5} needs to be determined by modeling, because there is no published value available from literature.

Assuming that only the protonated surface site α (denoted as \underline{S}_1) is responsible for the adsorption of three negatively charged arsenic species, denoted as $[\underline{S}_1OH_2^+] = \alpha_+ S_T$, where S_T is the total concentration an site α , and α_+ is the

fraction of the protonated surface site, then: $\alpha_+ = \frac{[H^+]}{[H^+] + K_H}$; The two neutral

calcium-arsenic species have no specific selectivity on the three surface sites. Therefore, all surface sites were normalized as one with a total site density of $[S_T]$ when considering the two neutral species. Adsorption of different arsenic species by surface sites can be expressed as:



where K_{S1} , K_{S2} , K_{S3} , K_{S4} and K_{S5} are adsorption constants of the five arsenic species, respectively. These are the parameters to determine by modeling.

The total soluble adsorbed arsenic concentration $[As(V)]_D$ and total adsorbed arsenic concentration $[As(V)]_{ads}$ can be expressed with the following equations:

$$[As(V)]_D = [H_3AsO_4] + [H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}] + [CaHAsO_4] + [Ca_{1.5}AsO_4] \quad (12)$$

$$[As(V)]_{ads} = [S_1-H_2AsO_4] + [S_1-HAsO_4^-] + [S_1-AsO_4^{2-}] + [S-CaHAsO_4] + [S-Ca_{1.5}AsO_4] \quad (13)$$

According to previous research, if the total adsorbate concentration (in M) is less than 10% of the surface site concentration, which is true in this study, then the adsorption is in the linear range of the Langmuir isotherm¹⁹, and the concentration of adsorbed species can be expressed as:

$$[S_1-H_2AsO_4] = K_{S1}[S_1OH_2^+][H_2AsO_4^-] \quad (14)$$

$$[S_1-HAsO_4^-] = K_{S2}[S_1OH_2^+][HAsO_4^{2-}] \quad (15)$$

$$[S_1-AsO_4^{2-}] = K_{S3}[S_1OH_2^+][AsO_4^{3-}] \quad (16)$$

$$[S-CaHAsO_4] = K_{S4}[S][CaHAsO_4] \quad (17)$$

$$[S-Ca_{1.5}AsO_4] = K_{S5}[S][Ca_{1.5}AsO_4] \quad (18)$$

The total arsenic concentration $[As(V)]_T$ in the system is:

$$[As(V)]_T = [As(V)]_D + [As(V)]_{ads}$$

Based on equations 2-18, $[As(V)]_D$ can be solved and expressed as:

$$[As(V)]_D = \frac{[As(V)]_T \times B}{B+C} \quad (19)$$

where,

$$B = \frac{1}{\alpha_0} + \frac{K_1 K_2 K_4 [Ca]}{[H]^2} + \frac{K_1 K_2 K_3 K_5 [Ca]^{1.5}}{[H]^3} \quad (20)$$

$$C = \alpha^+ [S_{1T}] \left(\frac{K_{S1} K_1}{[H]} + \frac{K_{S2} K_1 K_2}{[H]^2} \right) + [S_T] \left(\frac{K_{S4} K_1 K_2 K_4 [Ca]}{[H]^2} + \frac{K_{S5} K_1 K_2 K_3 K_5 [Ca]^{1.5}}{[H]^3} \right) \quad (21)$$

$$\alpha_0 = \frac{[H]^3}{[H]^3 + [H]^2 K_1 + [H] K_1 K_2 + K_1 K_2 K_3} \quad (22)$$

Equation 19 and the nonlinear regression function of SigmaPlot sigma were used to model experimental data $As(V)_D$ as a function of pH and $[Ca]$, and to determine the values of constants K_5 , K_{S1} , K_{S2} , K_{S4} and K_{S5} . Modeling results are listed in Table 4 together with the standard error and R^2 . Soluble arsenic concentrations predicted by the adsorption model are also plotted in Figure 3 as solid lines. The good agreement between experimental and modeling results suggested the validity of the developed model for this dataset.

CONCLUSIONS

This research demonstrated that different arsenic leaching behaviors from acidic and alkaline fly ashes were correlated with the calcium content in bulk ash, and a calcium phase was likely to be responsible for the stabilization of arsenic in the alkaline pH range. As(V) adsorption on to acidic fly ash was significantly enhanced by added calcium under basic conditions. Solubility product calculation indicated that this process was not controlled by precipitation of $\text{Ca}_3(\text{AsO}_4)_2$. Instead, it is hypothesized that calcium complexes with arsenic and forms two neutral species CaHAsO_4 and $\text{Ca}_3(\text{AsO}_4)_2$ which have a relatively high affinity for fly ash surfaces at high pH, resulting in increased arsenic adsorption. The adsorption model developed in this study successfully predicted As(V) adsorption behavior on an acidic ash #1008, and the formation and adsorption constants of different arsenic species were determined.

ACKNOWLEDGEMENTS

This work was supported by the Electric Power Research Institute (EPRI) and the Environmental Research Center (ERC) for Emerging Contaminants at the University of Missouri-Rolla (UMR). The authors also gratefully acknowledge Mr. Shi Shu at University of Missouri-Rolla for his contribution to the leaching experiment and chemical analysis; and Dr. C.P. Huang and Mr. Minghua Li at the University of Delaware for providing the zeta potential measurement. Conclusions and statements made in this paper are those of the authors, and in no way reflect the endorsement of the aforementioned funding agencies.

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Table 1. Sample characterization.

Sample ID	Coal Type	Natural pH (S/L = 1:10)	As (mg/kg)	Ca (%)	BET Area (m ² /g)	pH _{pzc}	LOI (%)
Ash #1005	Bituminous	5.5	44.9	0.50	18.43	6.2	12.7
Ash #1004	Bituminous	4.5	49.0	0.59	7.57	6.4	6.7
Ash #1008	Bituminous	6.5	139.4	1.11	6.48	6.2	8.5
Ash #1009	Bituminous	6.0	100.9	1.0	8.71	7.4	9.8
Ash #1015	Subbituminous	10.6	37.2	14.3	25.65	7.6	14.8
Ash #1018	Subbituminous	10.6	52.1	12.98	15.68	6.8	9.7
Ash #7	Subbituminous	12.3	29.1	16.15	1.24	6.6	0.2

Table 2. Ion product of $[Ca]^{3} \times [AsO_4]^{2}$ (with 50 mg/L of Ca addition).

pH	$[Ca]^{3} \times [AsO_4]^{2}$
8.00	3.22E-25
9.15	8.79E-23
10.25	9.51E-22
10.70	1.16E-21
11.88	1.17E-21

Table 3. Surface site densities and acidity constants for ash #1008.

Surface Site Parameters	α	β	γ
Γ (10 ⁻⁵ mol/g)	44 ± 1.4	3.6 ± 1.6	5.4 ± 2.0
pK _H	3.2 ± 0.1	7.3 ± 0.5	11.3 ± 0.9

Table 3. Modeling results for arsenic partitioning with ash #1008.

Arscopic Species	H ₂ AsO ₄	HAsO ₄	CaHAsO ₄	Ca _{1.5} (AsO ₄)	R ²
Formation Constant (logK)	/	/	/	4.7 ± 0.7	0.89
Adsorption Constant (logKs)	2.6 ± 0.1	7.2 ± 0.2	1.9 ± 0.2	2.6 ± 0.5	

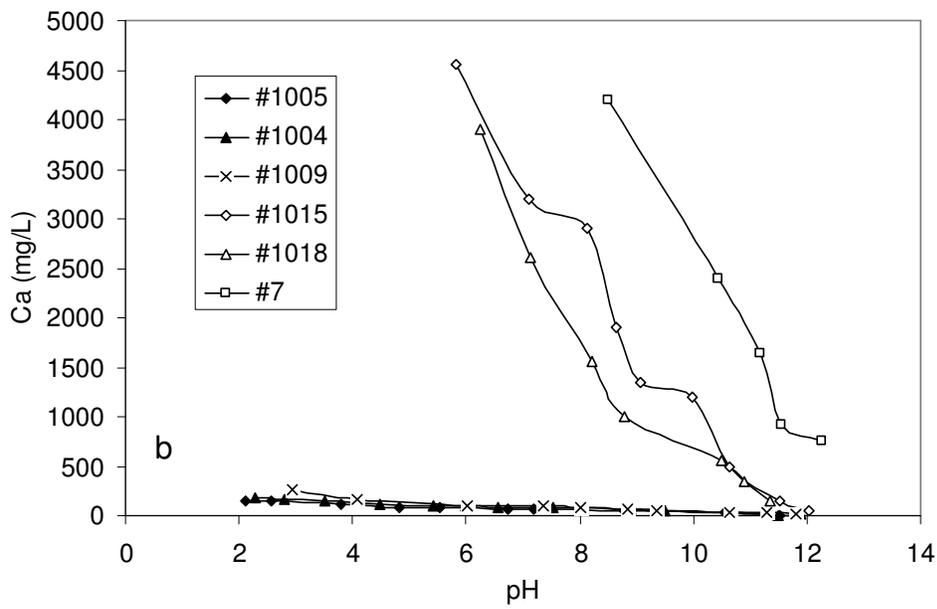
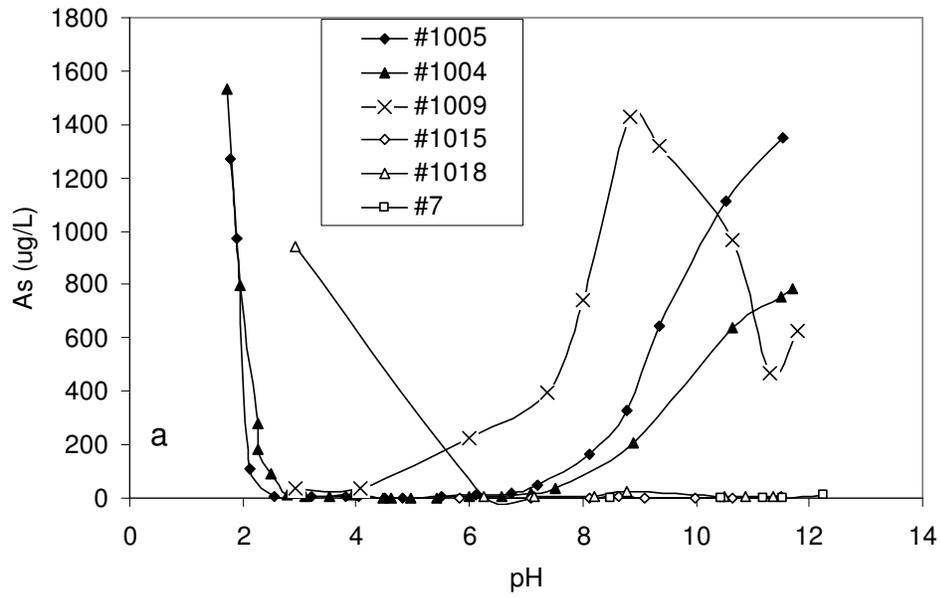


Figure 1. (a) As, (b) Ca leaching from acidic and alkaline coal fly ashes. Experimental conditions: S/L = 1:10; temperature = 20 – 25 °C; equilibration time = 24 hours.

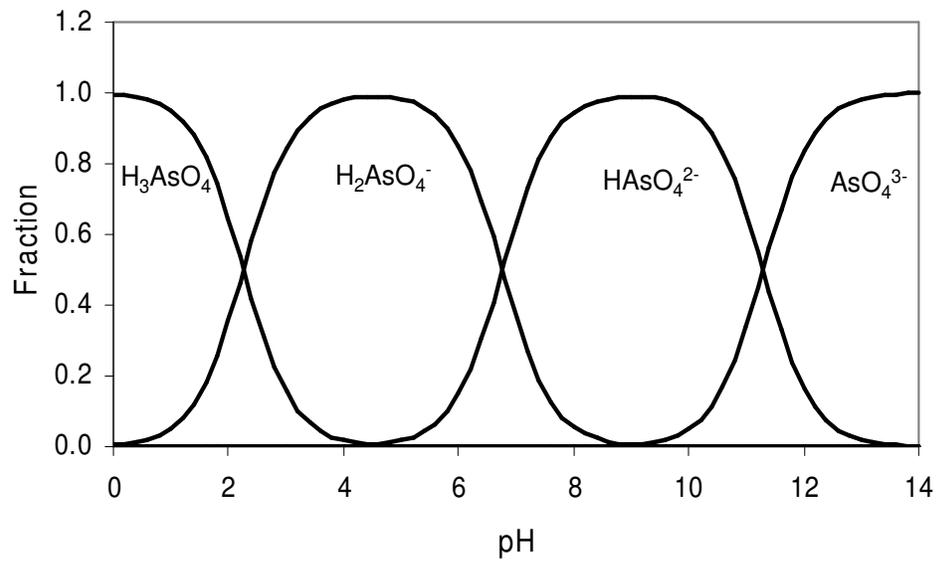


Figure 2. Speciation of arsenic acid.

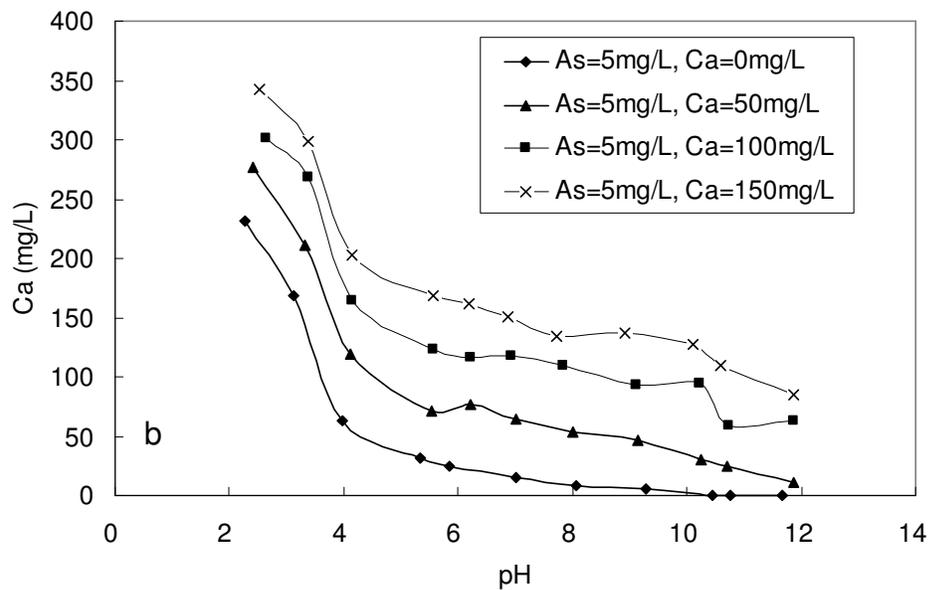
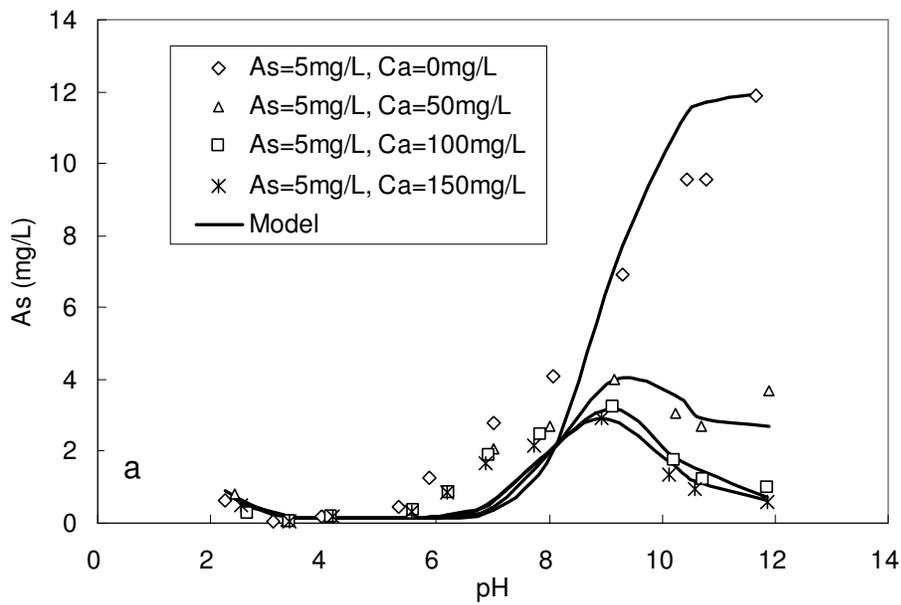


Figure 3. Arsenic partitioning for fly ash #1008 with and without addition of Ca: (a) Arsenic concentration as a function of pH; (b) Calcium concentration as a function of pH

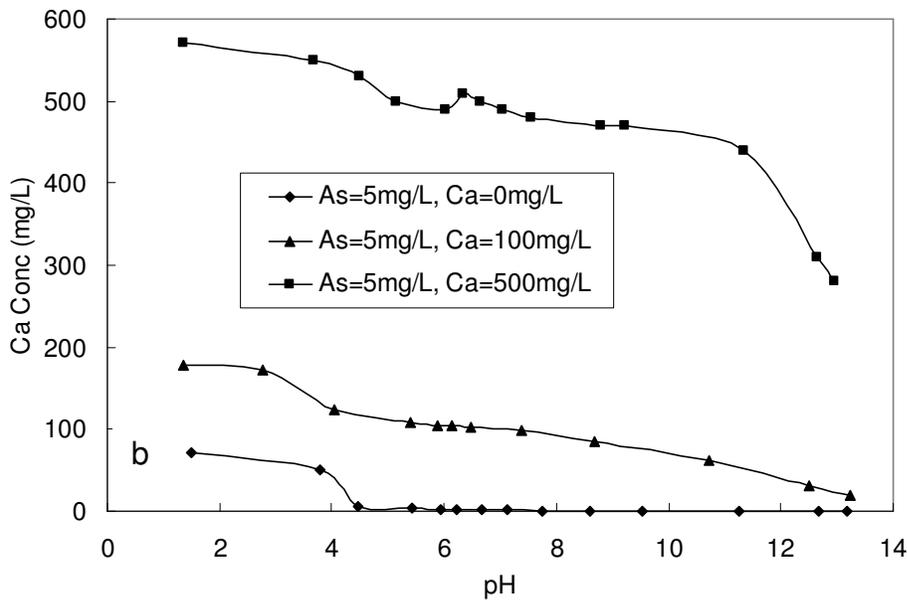
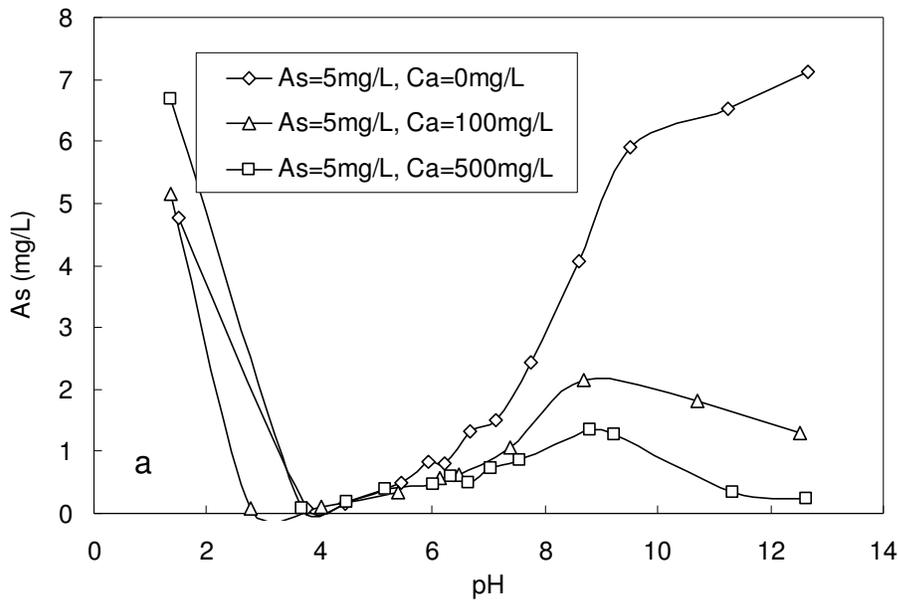


Figure 4. Arsenic partitioning for fly ash #1005 with and without addition of Ca: (a) Arsenic concentration as a function of pH; (b) Calcium concentration as a function of pH.

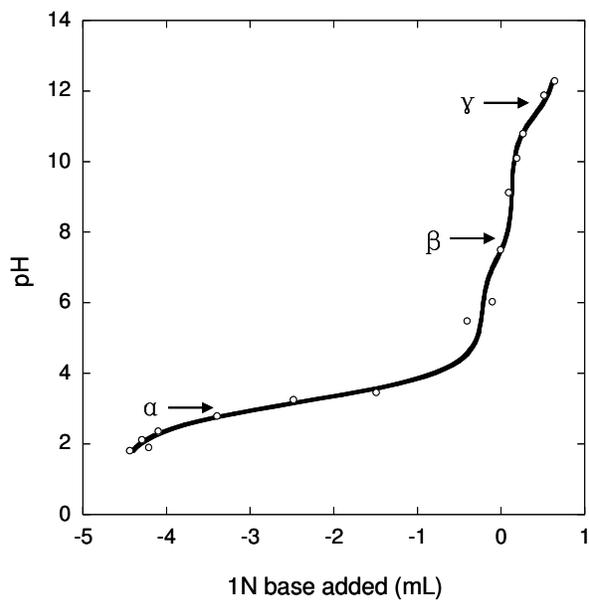


Figure 5. Titration and curve fitting results for Ash #1008. Experimental conditions: S/L = 1:10; ionic strength = 0.01 M (NaNO_3); temperature = 20 – 25 °C; equilibration time = 24 hours